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Catalytic Coupling of sp^2- and sp-Hybridized Carbon–Hydrogen Bonds with Vinylmetalloid Compounds

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ABSTRACT

In the Account given herein, it has been shown that silylative coupling of olefins, well-recognized as a new catalytic route for the activation of =C–H bond of olefins and =C–Si bond of vinylsilicon compounds with ethylene elimination, can be extended over both other vinylmetalloid derivatives (=C–E) (where E = Ge, B, and others) as well as the activation of ≡C–H, =C$_{\text{aryl}}$–H, and –O–H bond of alcohols and silanols. This general transformation is catalyzed by transition-metal complexes (mainly Ru and Rh) containing or initiating TM–H and/or TM–E bonds (inorganometallics). This new general catalytic route for the activation of =C–H and ≡C–H as well as =C–E bonds called metallative coupling or *trans*-metalation (cross-coupling, ring-closing, and polycondensation) constitutes an efficient method (complementary to metathesis) for stereo- and regioselective synthesis of a variety of molecular and macromolecular compounds of vinyl–E (E = Si, B, and Ge) and ethynyl–E (E = Si and Ge) functionality, also potent organometallic reagents for efficient synthesis of highly π-conjugated organic compounds. The mechanisms of the catalysis of this de-ethenative metalation have been supported by equimolar reactions of TM–H and/or TM–E with initial substances and reactions with deuterium-labeled reagents.

1. Introduction

Organic derivatives of metalloids, such as silicon, boron, and germanium, make a group of the so-called organometallic compounds. However, these metalloids (*p*-block elements) can also replace the carbon atom in metal–carbon bonding, forming real metal–nonmetal bonding. Such compounds are the subjects of a new field of study called “inorganometallic chemistry”.[1,2] The triangle (Figure 1) illustrates the relation between organometallic (mainly organotransition-metal), hetero-organic, and inorganometallic chemistry.

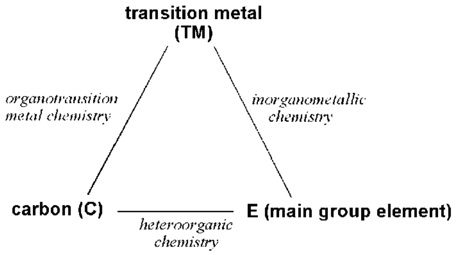
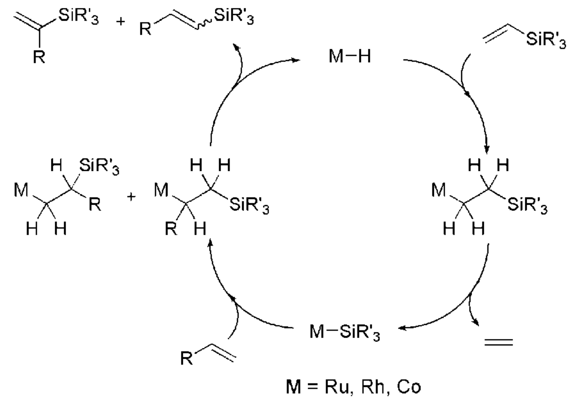


FIGURE 1. Relation between organotransition-metal, hetero-organic, and inorganometallic chemistry.

Scheme 1



The formation and breaking of the transition-metal–carbon (TM–C) bond plays a decisive role in catalytic reactions of organic compounds, which, in the second half of the 20th century, became a milestone in synthetic organic chemistry. On the other hand, the reactivity of inorganometallic species, particularly those involving the transition-metal *p*-block metal (TM–E) bond, is of key importance in most conversions of the *p*-block element derivatives catalyzed by TM complexes (for a recent review, see ref 2). They lead to selective synthesis of a variety of hetero-organic and organometallic molecular and macromolecular compounds forming a carbon–heteroatom (C–E) bond, such as hydrometalation (hydrosilylation, dehydrogenative silylation, hydrostannylation, hydroboration, and hydrophosphinylation) and bismetalation, as well as E–E and E–E′ bonds, e.g., dehydrocoupling. The results of mechanistic studies indicate that such processes proceed in the presence of catalytic species containing initially or generated in situ TM–H and TM–E bonds. All of the final products of such transformations, i.e., those involving the E–C, E–E, and E–E′ bonds, play a fundamental role in advanced organic and polymer synthesis, particularly if followed by the cross-coupling reactions with organic fragments, usually catalyzed by palladium complexes.

In the last 2 decades, we have developed a new type of TM-catalyzed reaction of vinyl-substituted organosilicon compounds with a variety of olefins, called the silylative coupling (SC) or *trans*-silylation, taking place in the presence of complexes containing or generating M–H and M–Si (silicometallics) bonds (for a recent review, see ref 3). While silylative coupling has become a very valuable synthetic tool in the preparation of vinyl-substituted organosilicon reagents and polymers, this mode of reactivity has been recently found to be general and also exhibited by vinyl derivatives of other *p*-block elements (e.g., boron and germanium). It has also been extended to catalytic activation by such vinylmetalloids (mainly vinylsilicon) as ≡C$_{\text{alkynyl}}$–H,[4] =C$_{\text{aryl}}$–H,[5] and even –O–H bond of alcohols[6] and silanols,[7] indicating a new general role of

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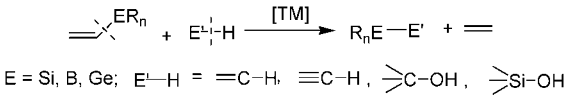
vinylmetalloid compounds as metalation agents and hydrogen acceptors. Thus, in this Account, we are presenting recent results on the general activation of mainly sp^2- and sp-hybridized carbon–hydrogen bonds by vinylmetalloid compounds $CH_2{=}CH{-}E$ catalyzed by TM (mainly Ru, Rh, Co, and Ir) complexes containing or generating M–H and M–E (inorganometallics) bonds. This reaction occurs according to the following general equation (eq 1):

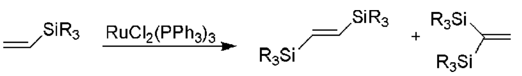


(1)

We also review the mechanistic aspects of all of the catalytic processes described, supported by equimolar reactions of TM–E with substrates and reactions with deuterium-labeled reagents. Additionally, we present application of these reactions to the synthesis of a variety of linear and cyclic organometalloid (mainly organosilicon) compounds as potent intermediates in organic synthesis and as precursors of optoelectronic materials.

2. Silylative Coupling (*trans*-Silylation) of Olefins with Vinylsilanes

In 1984, we reported the first effective example of self-metathesis (disproportionation) of vinyl-substituted silicon compounds catalyzed by ruthenium complexes (eq 2)



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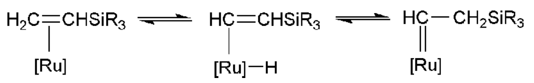
It opened a new route of great synthetic importance and allowed us to synthesize a series of unsaturated silicon compounds in high yield (>70%) (for a review, see refs 3 and 8).

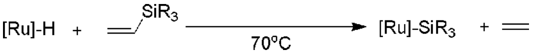
Experiments performed at that time with ill-defined catalysts did not distinguish between the reaction involving ruthenium carbene intermediates and/or the nonmetallacarbene mechanisms. We assumed the following mode of generation of carbene complexes in ruthenium precursor/vinylsilane systems (eq 3):



$$\underset{[Ru]}{H_2C{=}CHSiR_3} \rightleftharpoons \underset{[Ru]{-}H}{HC{=}CHSiR_3} \rightleftharpoons \underset{[Ru]}{\overset{}{HC}{-}CH_2SiR_3} \qquad (3)$$

Subsequent experiments have shown that, in the reaction referred to as "the metathesis" of vinylsilanes, instead of the C=C bond cleavage (formally characterizing alkene metathesis), the silylative coupling takes place in the presence of complexes containing or generating M–H and M–Si bonds (where M = Ru, Rh, Co, and Ir).

The mechanisms of silylative coupling proposed by Wakatsuki et al.[9] (corrected for Ru complexes by our group[10]) and proposed for other metal complexes, such as Rh[11] and Co,[12] proceeded via insertion of vinylsilane into the M–H bond and β-Si transfer to the metal with elimination of ethylene to generate M–Si species, followed by insertion of alkene (vinylsilanes in homocoupling) and β-H transfer to the metal with elimination of substituted vinylsilanes (Scheme 1). The insertion–elimination mechanism of catalysis has been supported by stoichiometric reactions of alkene and vinylsilane with Ru–Si, Rh–Si, Co–Si, and Ru–H bonds (e.g., see eqs 4–9).[9,10a,b,11–13]



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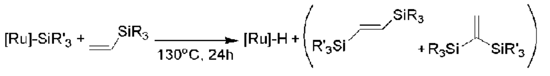

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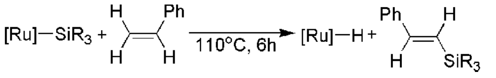

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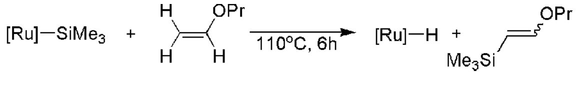

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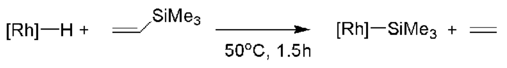

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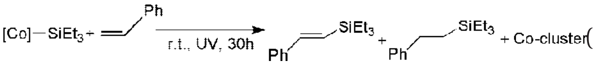
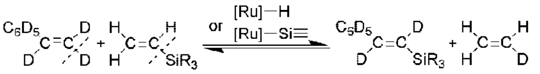


(9)

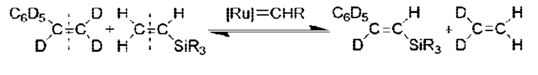
The detailed mechanism of silylative coupling of functionalized alkenes, such as styrene,[10b] vinyl alkyl ethers,[13] vinylamides,[14] and vinylboronates,[15] catalyzed by ruthenium complexes containing the Ru–H or Ru–Si bond ($RuHCl(CO)(PPh_3)_3$, $RuHCl(CO)(PCy_3)_2$, $RuHCl(CO)(PCy_3)_2$/CuCl (1:3), $RuCl(SiMe_3)(CO)(PPh_3)_2$, and $RuCl(SiMe_2Ph)(CO)(PPh_3)_2$), has also been subsequently presented.

The mechanism of catalysis of the silylative coupling versus cross-metathesis has been finally supported by a new diagnostic tool introduced in 1997,[10b] i.e., using mass spectrometry to study the products of deuterated alkene, e.g., styrene, vinyl alkyl ether, and/or deuterated vinylsilane. For example, see[10b]



(10)

If the reaction occurs via the insertion–elimination mechanism (silylative coupling), the silylstyrene-d_7 containing only a deuterium label in the molecule is formed (e.g., eq 10). However, if the reaction proceeds according to the metallacarbene mechanisms (cross-metathesis), the process described above takes place (eq 11). The gas chromatography–mass spectrometry (GC–MS) study of the reactions examined in the first stage (10% of the conversion) shows the exclusive formation of the silylation product, which strongly supports the *trans*-silylation mechanism.



(11)

A quantum chemical approach based on density functional theory (DFT) calculations has been carried out to examine the mechanism of SC, leading to ethylene evolution using the model [Ru]–H/$CH_2{=}CHSiMe_3$ system.[16] The obtained results suggest that, depending upon the actual nature of substituents attached to the vinyl moiety or Si atom, the rate-determining step can be governed by the insertion of an

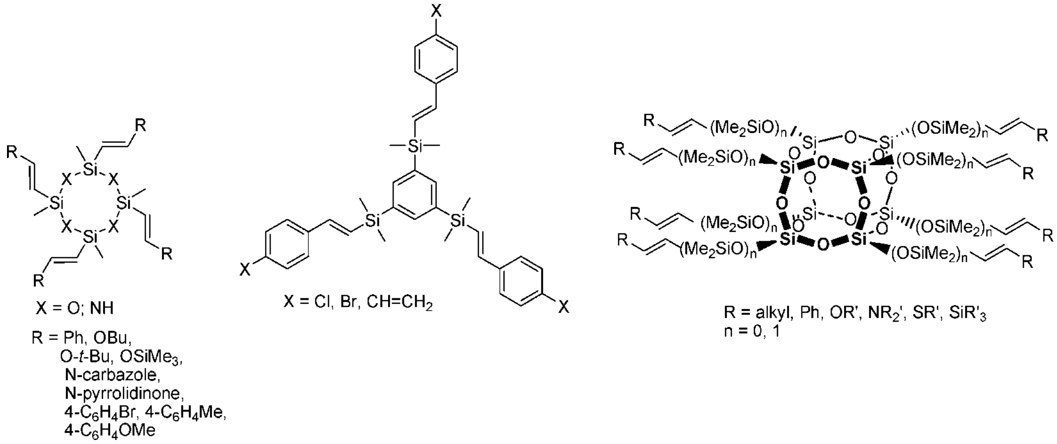
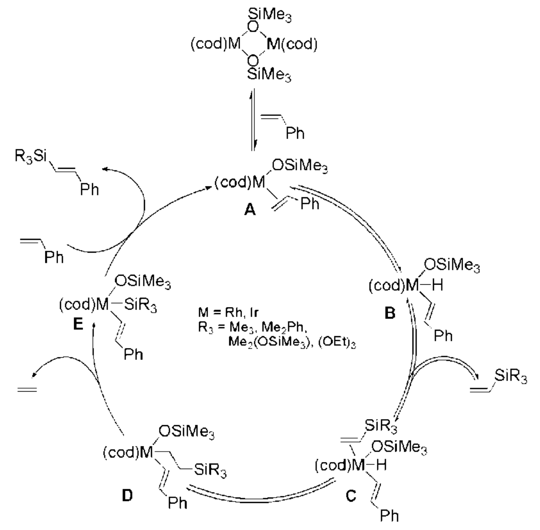


FIGURE 2. Multivinylsubstituted organosilicon compounds as products of SC condensation.

alkene into the Ru–Si bond coupled with the silyl moiety migration from Ru to C atoms or, alternatively, the reverse reaction, i.e., alkene elimination from the β-silylethyl ruthenium complex (see Scheme 1). In our calculations, optimized using DFT with a B3LYP basis set on model systems, the energy barriers were 16.5 and 15.3 kcal/mol for the forward and reverse reactions, respectively. However, the possibility of removing gaseous ethylene from the reactive mixture together with the entropic factors suggests that the insertion of alkene that is larger than C_2H_4 is the rate-limiting step in the silylative coupling of olefins. It also suggests that the substituents attached to the silicon atom or the carbon atoms of an alkene by electronic and steric effects may significantly affect silyl migration and thus the effectiveness of the catalytic reaction. Interestingly, both catalytically active species, [Ru]–H and [Ru]–$SiMe_3$, have similar energy, which agrees well with the experimental finding that the ruthenium complexes with –H or –SiR_3 ligands in the first coordination sphere of ruthenium are almost equally efficient in the catalytic process.

Rhodium and iridium siloxide complexes, such as $[(cod)Rh(OSiMe_3)]_2$ and $[(cod)Ir(OSiMe_3)]_2$, as precursors initially having no M–H have also been tested in the reaction of styrene and *p*-styrenes with various vinyl-substituted silicon compounds.[17a,b] Some experiments with deuterium-labeled reagents have shown the exclusive formation of silylstyrene-d_7 (see eq 10). Besides, the experiments on the reaction between d_0 and styrene d_8 tested in the presence of the catalytic amounts of both complexes have evidence that the H/D exchange has taken place via the M–H/M–D complexes. All of these experiments[17a,b] as well as the experiments performed previously by Brookhart and co-workers with the use of $C_5Me_5Rh(CH_2{=}CHSiMe_3)_2$[17c] have allowed us to propose a general mechanism of catalysis by rhodium and iridium siloxide complexes, summarized in Scheme 2 (for a review, see ref 18). The conclusion is that, if the catalysts contain initially no M–H and M–Si bond, their formation occurs via the oxidative addition of C_{vinyl}–H of alkene to generate the M–H bond (A → B), followed by coordination and insertion of vinylsilane to this bond (B → C → D). Next, β-Si transfer to the metal in complex D occurs with the elimination of ethylene (D → E), followed by reductive elimination of substituted vinylsilane (E → A) and regeneration of the catalyst.

Scheme 2

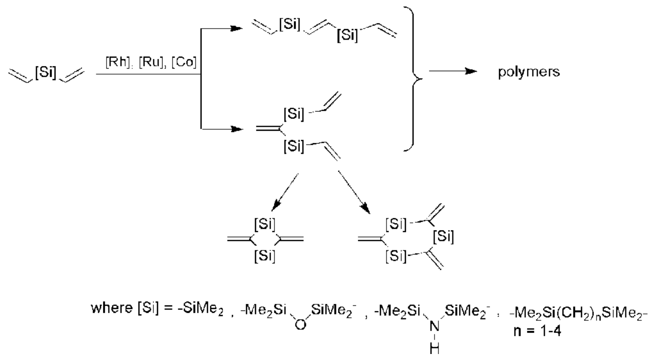


M = Rh, Ir
R_3 = Me_3, Me_2Ph, $Me_2(OSiMe_3)$, $(OEt)_3$

Divinyl-substituted silanes, siloxanes, and silazanes also undergo efficient silylative coupling in similar fasion to monovinylsilicon compounds. These disubstituted compounds undergo polycondensation to afford linear oligomers or cyclic dimers and trimers containing *exo*-cyclic methylene bonds (Scheme 3). The unique feature of this silylative coupling, distinguishing this reaction from cross-metathesis, is the formation of a 1,1-bis(silyl)ethene fragment in given conditions.

In the presence of $[RuCl_2(CO)_3]_2$ as a catalyst, *trans*-bis(vinylsilyl)ethenes are exclusively formed but $[(cod)RhX]_2$ (where X = Cl and $OSiMe_3$) catalyzes mostly the formation of *gem*-dimeric products. Ruthenium phosphine complexes give both types of products. The *gem* products subsequently undergo intramolecular ring closure to yield cyclic carbosiloxane, carbosilazane and carbosilane. Cyclization has been also reported to furnish cyclocarbosilanes with one exocyclic methylene group. Under the optimum conditions, silylative-coupling (poly)condensation in the presence of ruthenium complexes containing or generating M–H and/or M–Si bonds gives linear well-defined (silylene, siloxylene, and silazanylene) vinylene as well as silylene–vinylene–phenylene oligomers (for reviews, see refs 3 and 19).

Scheme 3



3. Synthetic Aspects of Silylative-Coupling Condensation and Polycondensation

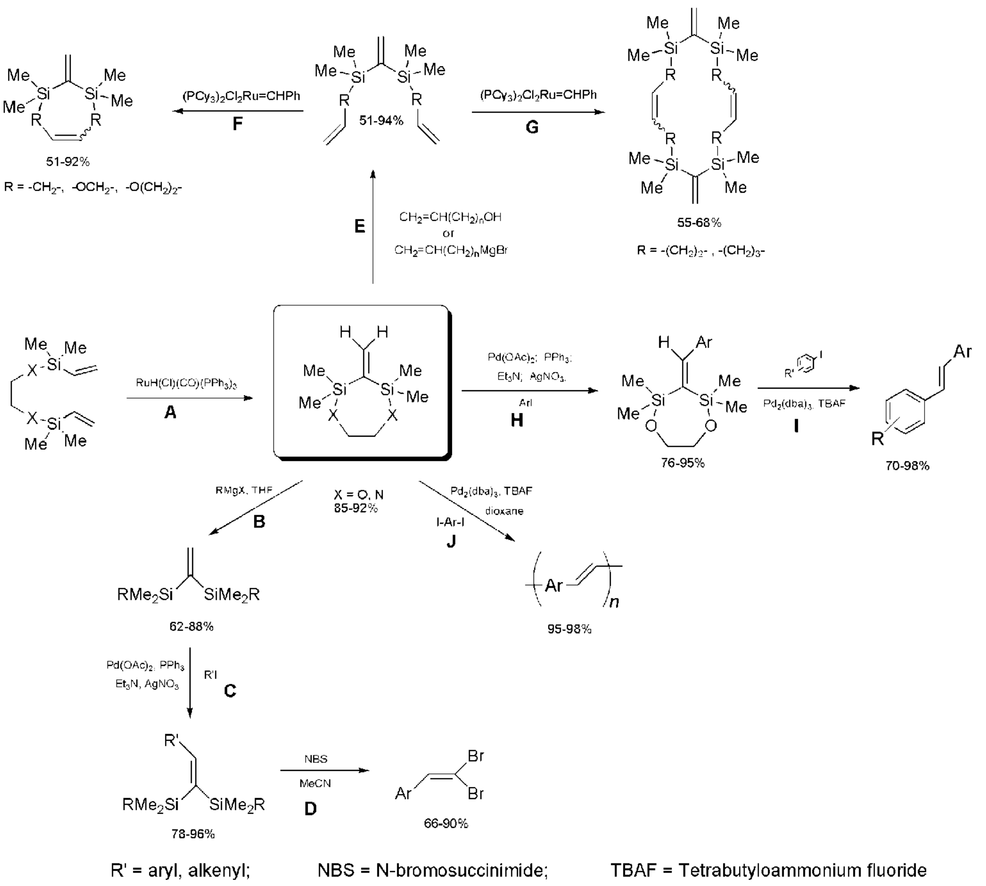
The silylative-coupling reaction as an alternative to cross-metathesis has been successfully applied to the synthesis of a variety of vinylsubstituted silyl olefins (for reviews, see refs 3 and 19) as well as multivinylsubstituted derivatives, such as 1,3,5-tris(dimethylvinylsilyl)benzene,[20] methylvinylcyclosiloxanes,[21] octavinylsilsesquioxanes,[22] and spherosilicates[23] (see Figure 2). Alkenylsilanes, particularly vinyl- and allylsilanes, make a class of organosilicon compounds commonly used in organic synthesis by providing suitable regio- and stereoselective routes.[24] The lack of toxicity, high chemical stabilities, and low molecular weight of organosilanes make them ideal compounds for palladium-catalyzed cross-coupling with organic halides and pseudohalides.[25]

In the course of our recent study of SC cyclization of divinyl-substituted organosilicon compounds, we have developed a new facile route for the synthesis of alkyl-, aryl-, alkenyl-, or alkoxy-substituted 1,1-bis(silyl)ethenes, which constitutes a specific class of alkenylsilanes (Scheme 4) (for a review, see ref 26).

One-pot silylative-coupling *exo*-cyclization of 1,2-bis(dimethylvinylsiloxy)ethane followed by the reaction with Grignard reagents leads to the desired 1,1-bis(silyl)ethenes.[27] Such compounds can be efficiently coupled in the presence of silver nitrate and palladium acetate with aryl or alkenyl iodides to give the corresponding 1,1-bis(silyl)-2-arylethenes or 1,1,4-trisubstituted 1,3-butadienes with high yield[28] (pathways A → B → C in Scheme 4). The easily accessible 1,1-bis(silyl)-2-arylethenes according to these procedures can be selectively converted to synthetically useful 1,1-dibromo-2-arylethenes using *N*-bromosuccinimide under mild conditions in good yields[29] (pathway D).

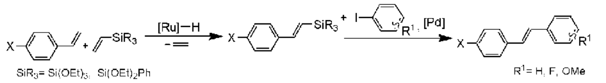
This de-ethenative silylative-coupling cyclization of divinyl-substituted monomers has also been used as a new facile and efficient route for the synthesis of dialkenyl- and dialkenyloxy-substituted 1,1-bis(silyl)ethenes (pathway E).[28] The products have been successfully converted into new silacyclic (pathway F) or silamacrocyclic (pathway G) olefins via ring-closing metathesis (RCM), using the first-generation Grubbs catalyst. The structures of both macrocyclic silaolefins have been confirmed using X-ray diffraction.[30]

Scheme 4



Bis(silyl)alkenes can also be effectively used in the sequential procedure for the synthesis of unsymmetrical stilbenes (pathways H and I) and arylene vinylene polymers (pathway J) in the palladium-catalyzed Hiyama reaction with monoiodo- and di-iodoarenes, respectively.[31]

A series of (*E*)-4-chlorostilbenes[32] (eq 12) and *p*-substituted (*E*)-*N*-styryl-carbazoles[33] (eq 13) via sequential silylative-coupling–Hiyama-coupling reactions have been synthesized in high yield and stereoselectivity. X-ray structures of the intermediate silylvinylcarbazole as well as some products have been obtained.[33]



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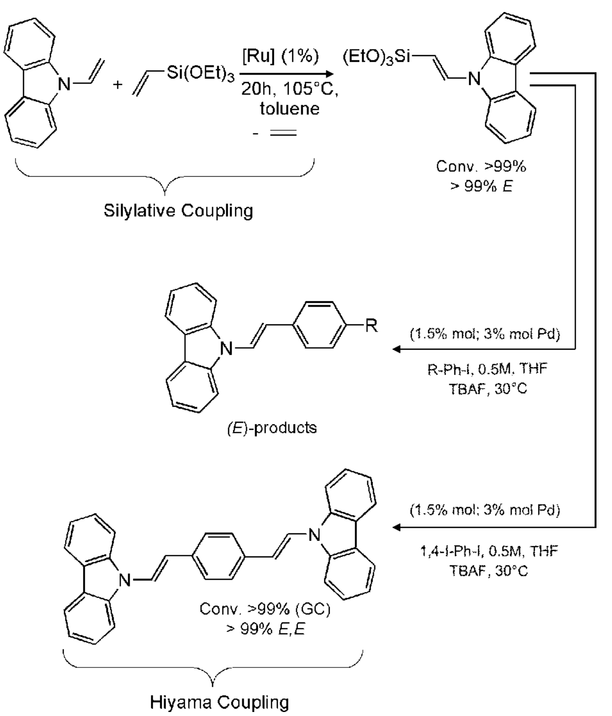


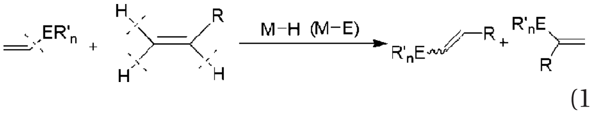
(13)

Conjugated polymers containing silylene and π-electron moieties are attractive because they afford processable optoelectronic materials and the silicon-based spacers interrupting the π-conjugated chains, resulting in unusual optical properties.[34] The first stereoregular *trans*-arylene–silylene–vinylene polymers [M_w = 13 100–34 800 and polydispersity index (PDI) = 1.6–2.9] can be effectively synthesized using just $RuH(Cl)(CO)(PCy_3)_2$-catalyzed SC, i.e., homopolycondensation of bis(vinyldimethylsilyl)arenes, cross-polycondensation of 4-(vinyldimethylsilyl)styrene, and copolycondensation of bis(vinyldimethylsilyl)-arenes with 1,4-divinylbenzene.[35] The structures of these polymers have been characterized and determined by ^1H, ^{13}C, and ^{29}Si nuclear magnetic resonance (NMR) as well as Fourier transform infrared (FTIR) spectroscopy (Figure 3). The absence of fragments with bis-silyl-substituted sp^2 carbon atoms ($Si_2C{=}CH_2$) in the chains of each polymer was also confirmed by distortionless enhancement by polarization transfer (DEPT) spectroscopic analysis. SC polycondensation opens a new synthetic route to regio- and stereoregular arylene–silylene–vinylene polymers (see also refs 8 and 19).

4. Activation of the Olefinic Carbon–Hydrogen Bond by Vinylmetalloid Compounds

As mentioned above, the silylative coupling (*trans*-silylation) has become a very valuable synthetic tool in the preparation of vinyl-substituted molecular and macromolecular organosilicon compounds. However, we have recently found that this mode of reactivity seems to be general and is also exhibited by vinylboronates, vinylgermanes, and perhaps, vinyl derivatives of other *p*-block elements.

The general scheme of these reactions is as follows (eq 14):



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The results of all mechanistic studies in which vinylsilicon, vinylboron, and vinylgermanium compounds were used have indicated that the process proceeds in the

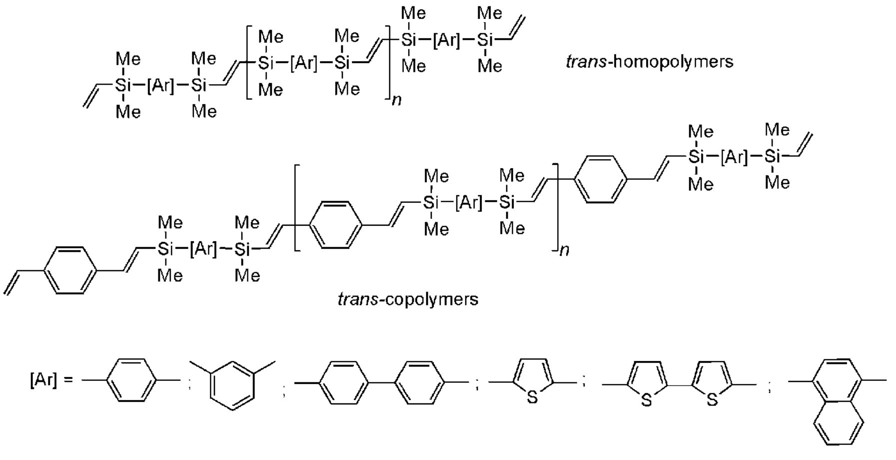
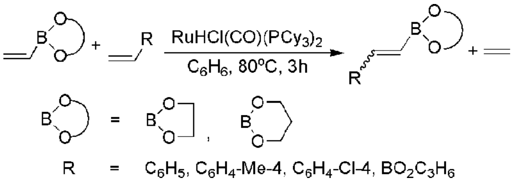


FIGURE 3. Stereoregular arylene–silylene–vinylene polymers.

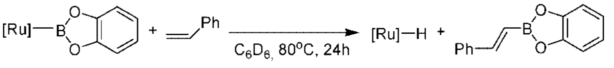
presence of catalytic species containing initially or generating in situ M–H and M–E bonds via cleavage of the =C–E and =C–H bonds of olefins.

trans-Borylation occurs in the presence of RuHCl(CO)(PCy$_3$)$_2$, according to the nonmetallacarbene mechanism and leads to the effective formation of the vinylborane derivative (eq 15).[36]



(15)

A stoichiometric study on the insertion of olefin into the Ru–B bond (eq 16) and a new experiment on the insertion of vinylborane into the Ru–H bond followed by the formation of the Ru–B bond and evolution of ethylene (eq 17) have been reported and provided convincing evidence for the nonmetallacarbene mechanism of the reaction observed.[36]



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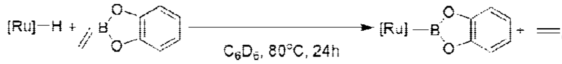
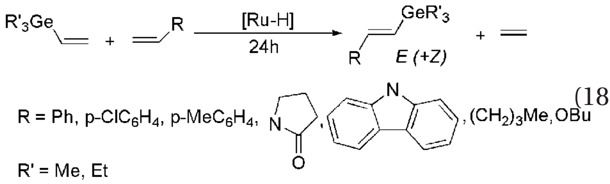


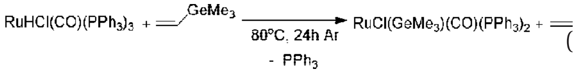
(17)

Ruthenium complexes RuHCl(CO)(PCy$_3$)$_2$ and RuHCl(CO)(PPh$_3$)$_3$ also catalyze the reaction of vinylgermanium compounds with selected alkenes >(*trans*-germylation), leading to the effective formation of vinylgermane derivatives that cannot be obtained via a cross-metathesis procedure (eq 18).[37]

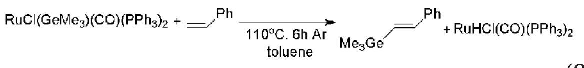


(18)

A separate equimolar study on the insertion of vinylgermane into the Ru–H (eq 19) bond as well as the insertion of styrene into Ru–Ge (eq 20) bonds have also supported the proposed mechanism.

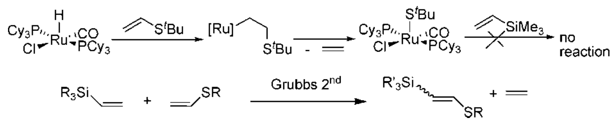


(19)



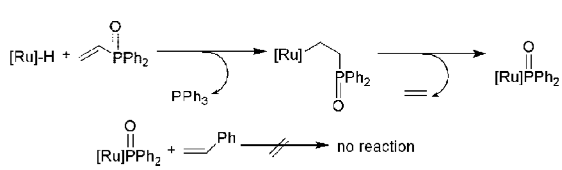
(20)

It has been assumed that the reaction of vinyl-substituted sulphur compounds can occur in the same manner. However, although the stoichiometric study of the Ru–H complex with vinylsulphides has shown the β-sulphur transfer to ruthenium with the evolution of ethylene, no olefin insertion has been observed in the next step; therefore, there is no catalytic coupling (eq 21).[38]



(21)

The same process is observed for vinyldiphenylphosphonate (eq 22).



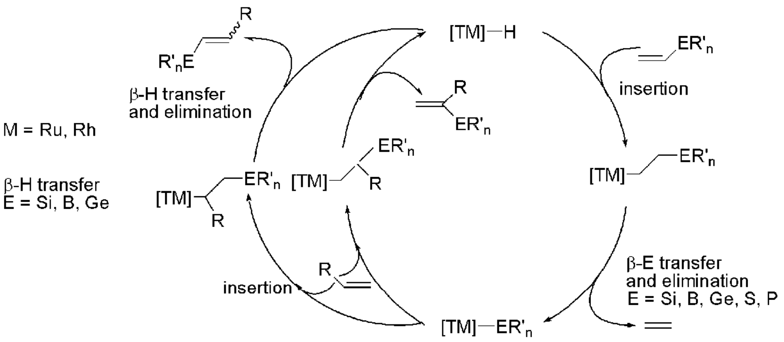
(22)

Finally, the general mechanistic scheme of this new type of *trans*-metalation involves the insertion of the vinyl-heteroatom into the M–H bond followed by β-E transfer with elimination of ethylene and the migratory insertion of alkenes or the vinylheteroatom compound (in the case of homocoupling) into the M–E bond followed by β-H elimination to give (organo)(heteroatom)-substituted ethenes (Scheme 5). While in the case of silicon, boron, and germanium, the total catalytic cycle proceeds, in the vinyl-S- and vinyl-P-containing compounds, only a half of this cyclic pathway is noted and thus, under the conditions studied, no catalysis is observed.

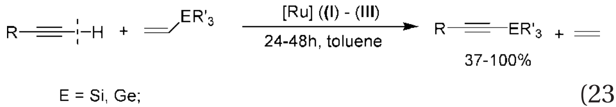
5. Catalytic Route for Activation of the sp-Carbon–Hydrogen Bond

Very recently, we have reported a new catalytic reaction that involves coupling of terminal alkynes with vinylsilicon compounds to get silylacetylenes.[4] This reaction opens a new catalytic route for the activation of the sp-hybridized C–H bond. As we have found previously for olefins, this reaction is also exhibited by vinylgermanes.[39] Therefore, the silylative (and germylative) coupling of alkynes proceeds in the presence of complexes containing [Ru]–H or [Ru]–Si and [Ru]–Ge bonds, e.g., RuHCl(CO)(PCy$_3$)$_2$ (I), Ru(SiMe$_3$)Cl(CO)(PPh$_3$)$_2$ (II), and Ru(GeEt)$_3$Cl(CO)(PPh$_3$)$_2$ (III), leading to the evolution of ethylene and formation of suitable silyl (or

Scheme 5



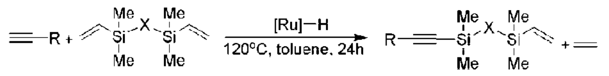
germyl) derivatives according to the following equation (eq 23):



E = Si, Ge;
R = alkyl, cycloalkyl, trialkylsilyl; trialkylgermyl, dimethylphenylsilyl
R' = alkyl, aryl, alkoxyl, siloxyl
[Ru] : [CH_2=CHER'$_3$] : [CH≡CR] = 1-2 x 10^{-2} : 2-10 : 1 (23)

While alkyl, cycloalkyl, and silyl (and germyl) ethynes were used efficiently in this process, the metalation of phenylacetylene does not occur. Selected results show a high yield and selectivity of respective alkynylsilanes (germanes) as main or exclusive products (TOF parameters measured after 0.5 h are equal to 16–58 h^{-1}).

Silylation of terminal alkynes by divinylsiloxanes and divinylsilazanes even at 6- or 10-fold excess of vinylsilicon compounds yields exclusively monoalkynylvinyldisiloxanes and -disilazanes with high yield and selectivity (eq 24) yet accompanied by a product of homocoupling of vinylsilicon substrates.



(24)

To provide evidence for the insertion of alkyne into the Ru–E bond, the catalysts containing a [Ru]–Si (II) and [Ru]–Ge (III) bond were subjected to an equimolar reaction with some alkynes, i.e., silylacetylene, germylacetylene, and phenylacetylene, to yield the respective main insertion product and ruthenium complexes (identified by GC–MS and ^{1}H NMR) spectroscopy (Scheme 6). [Ru]–H (IV–VI) complexes are apparently products of the insertion of acetylenes into the complex [Ru]–ER$_3$ in all experiments, but it could be detected at low temperature only in the case of the insertion of silyl- and germyl-acetylenes but not phenylacetylene. However, in the absence of the vinylmetalloid compound, these complexes are active in the hydrogenation of acetylene as well as in its respective dimerization or co-dimerization with styrene as a result of the well-known reaction catalyzed by ruthenium complexes.[40] All of the byproducts were detected and identified by GC and GC–MS. However, in contrast to the equimolar study under catalytic conditions (100–120 °C), vinylmetalloid, particularly if added in excess, reacts preferentially with ruthenium hydride species according to a well-documented process to yield a [Ru]–E complex and ethylene, which explains the catalytic activity of both [Ru]–H and [Ru]–E systems in the metallative coupling of alkynes. Apparently, in the case of phenylacetylene, its reaction with [Ru]–H proceeds more readily than with [Ru]–E, giving a vinylene complex and, therefore, there is no metalation of phenylacetylene under the conditions studied.

All of the experimental results have allowed us to propose a reasonable mechanism for the reaction with the vinylmetalloid compound with terminal acetylenes. The mechanistic scheme involves an insertion of alkynes (via a route proposed earlier)[41] into the [Ru]–E (E = Si and Ge) bond followed by β-H elimination to give substituted alkynes and, subsequently, the well-known insertion of the vinylmetalloid compound into the [Ru]–H bond followed by β-E elimination of ethylene. Dissociation of phosphine is postulated to generate the active Ru catalysts (Scheme 7).

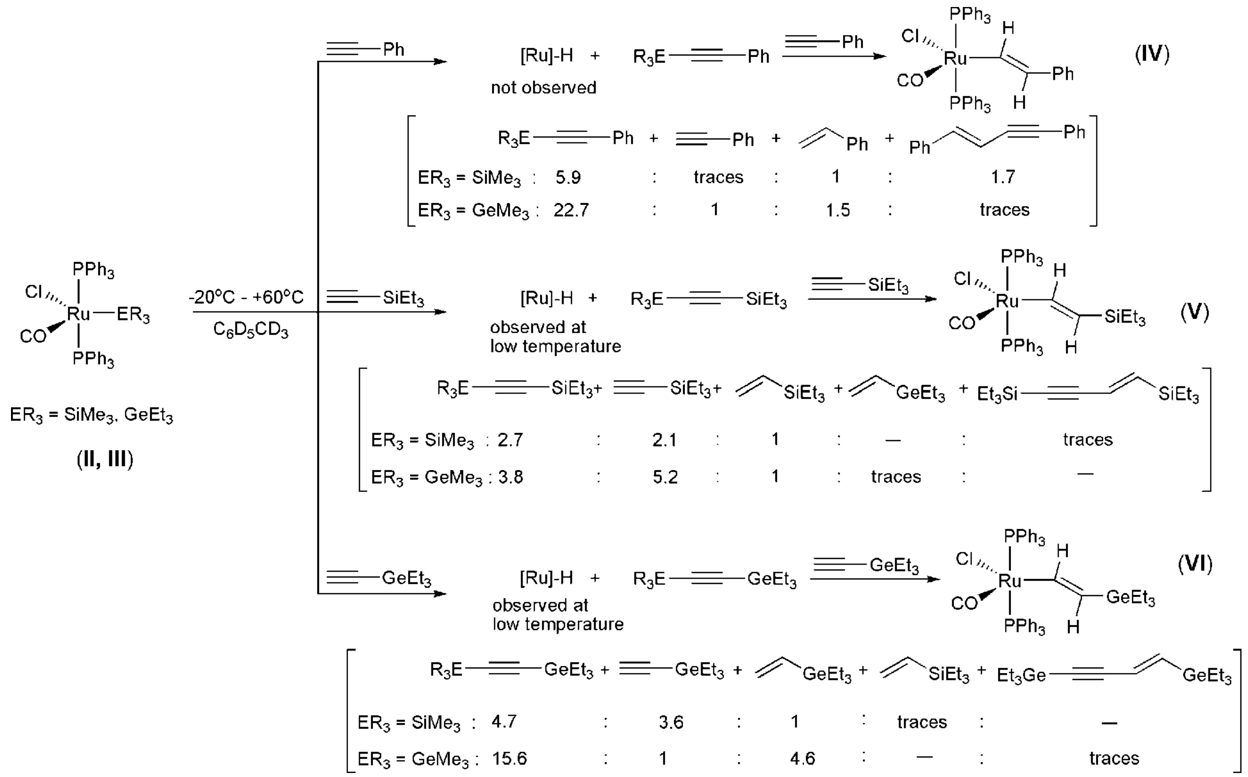
Very recently, we have also found that the activation of sp-C–H by the vinylsilicon compound also occurs in the presence of rhodium complexes containing no Rh–H or Rh–Si bonds initially;[4b] therefore, presumably, it can proceed via the respective mechanistic pathway well-documented for silylation of olefins.[8]

6. Other Examples of Vinylsilicon Compounds Acting as Metalation Agents and Hydrogen Acceptors

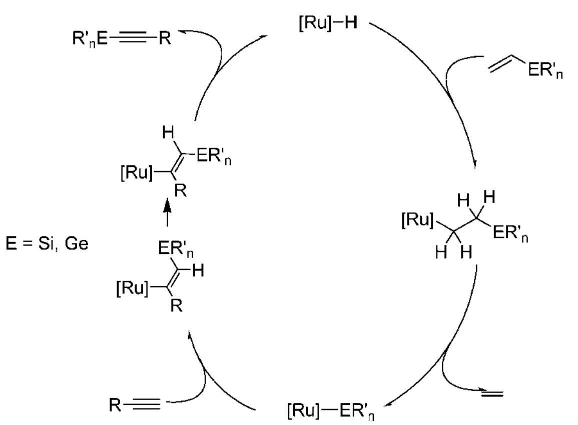
Beside catalytic activation of the olefinic and acetylenic carbon–hydrogen bond by vinylsilicon compounds, a few examples of their other coupling reactions with C–H and –O–H occurring in the presence of Rh and Ru complexes containing or generating M–H bonds have been recently reported.[5–7]

The catalytic activation of =C–H bond in aromatic ketones, esters and amines by vinylsilanes has been well-recognized by Murai et al., but these authors have also recently reported a Ru$_3$(CO)$_{12}$-catalyzed de-ethenative

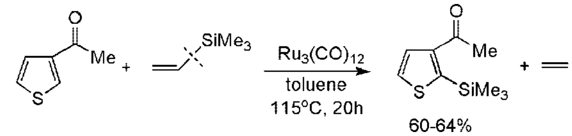
Scheme 6



Scheme 7

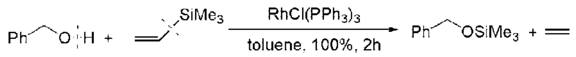


coupling (silylation) of 3-acetylthiophene with trimethylvinylsilane occurring as follows (eq 25):[5]



(25)

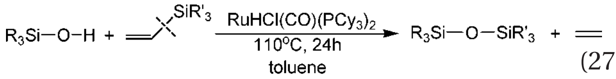
On the other hand, O-silylation of benzyl alcohol by vinylsilane occurs in high yield and selectivity in the presence of a Wilkinson catalyst (eq 26).[6]



(26)

The proposed mechanism involves an oxidative addition of alcohol to rhodium to give benzyloxy rhodium(III) hydride followed by insertion of vinylsilane into the Rh–H bond and β-silyl elimination of the resulting β-silylethyl rhodium(III) complex to give a silyl ether and ethylene.

Our preliminary experiments on the silylation of silanols by vinylsilanes has permitted us to reveal the following new reaction occurring in the presence of the ruthenium catalyst and yielding siloxanes and eliminating ethylene (eq 27):[7]



(27)

$R_3 = Pr_3, Me_2Ph, (OSiMe_3)_3$; $R'_3 = Me_2Ph, (OSiMe_3)_3, Me_3$

All of the examples mentioned confirm the new role of vinylsilicon (and presumably other vinyl metalloid compounds) as metalation agents and a hydrogen acceptor.

7. Concluding Remarks and Perspectives

The silylative coupling of olefins well-recognized as an efficient catalytic activation of the =C–H bond of olefins and =C–Si bond of organosilicon compounds can be extended over other metalloids (e.g., B and Ge) as well as over the activation of other sp^2- and sp-hybridized $=C_{aryl}$–H bonds and/or O–H bonds of alcohols and silanols.

The mechanism of this new catalytic activation of =C–H and ≡C–H bond has been proven to involve the insertion of vinyl-E into the TM–H (where TM = Ru, Rh, and Co) bond and β-E transfer to the metal with elimination of ethylene and generation of a TM–E bond followed by the insertion of alkene or alkyne into the TM–E bond and β-H transfer to the metal to eliminate silyl(germyl, boryl)ethene or the substituted silyl (germyl)ethyne, respectively.

If the catalyst (M = Ru, Rh, and Ir) contains initially no M–H and M–E bonds, their formation occurs via the oxidative addition of ═C–H and ≡C–H (also –O–H of the substrate in the case of alcohols and silanols) to generate M–H bonds followed by insertion of vinylmetalloid (CH_2═CH–E) compounds to this bond and, next, β-E transfer to the metal with elimination of ethylene followed by reductive elimination of respective substituted vinyl (or acetylenic) metalloid compounds (or alkoxysilanes and siloxanes).

This general catalytic route particularly for the activation of ═C–H as well as ≡C–E bonds, termed as metallative coupling (or *trans*-metalation) (cross-coupling, ring-closing, and polycondensation), constitutes an efficient method (complementary to metathesis) for stereo- and regioselective synthesis of a variety of molecular and macromolecular compounds of vinyl-E (E = Si, B, and Ge) as well as ethynyl-E (E = Si and Ge) functionality. Tandem (i.e., sequential) silylative-coupling–cross-coupling reactions can be used as new efficient routes for the synthesis of highly π-conjugated functionalized organic and organosilicon compounds.

Recent experiments on a catalytic activation of ═C_{aryl}–H, ≡C–O–H, and ≡Si–O–H bonds emphasize that vinylsilicon compounds function as silylating agents and hydrogen acceptors. Therefore, in view of all of the results discussed, this new catalytic route can be in the future extended to the general catalytic method for metalation of compounds containing carbon–hydrogen and heteroatom–hydrogen bonds by vinylmetalloid compounds.

My warmest thanks are due to the talented co-workers whose names appear in the references. This work was supported by the projects of the Ministry of Science and High Education numbers PBZ-KBN 118/T09/17 and N204 162 32/4248.

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